John E. McMurry • Robert C. Fay

General Chemistry: Atoms First

Chapter 3
Periodicity and the Electronic Structure of Atoms

Lecture Notes

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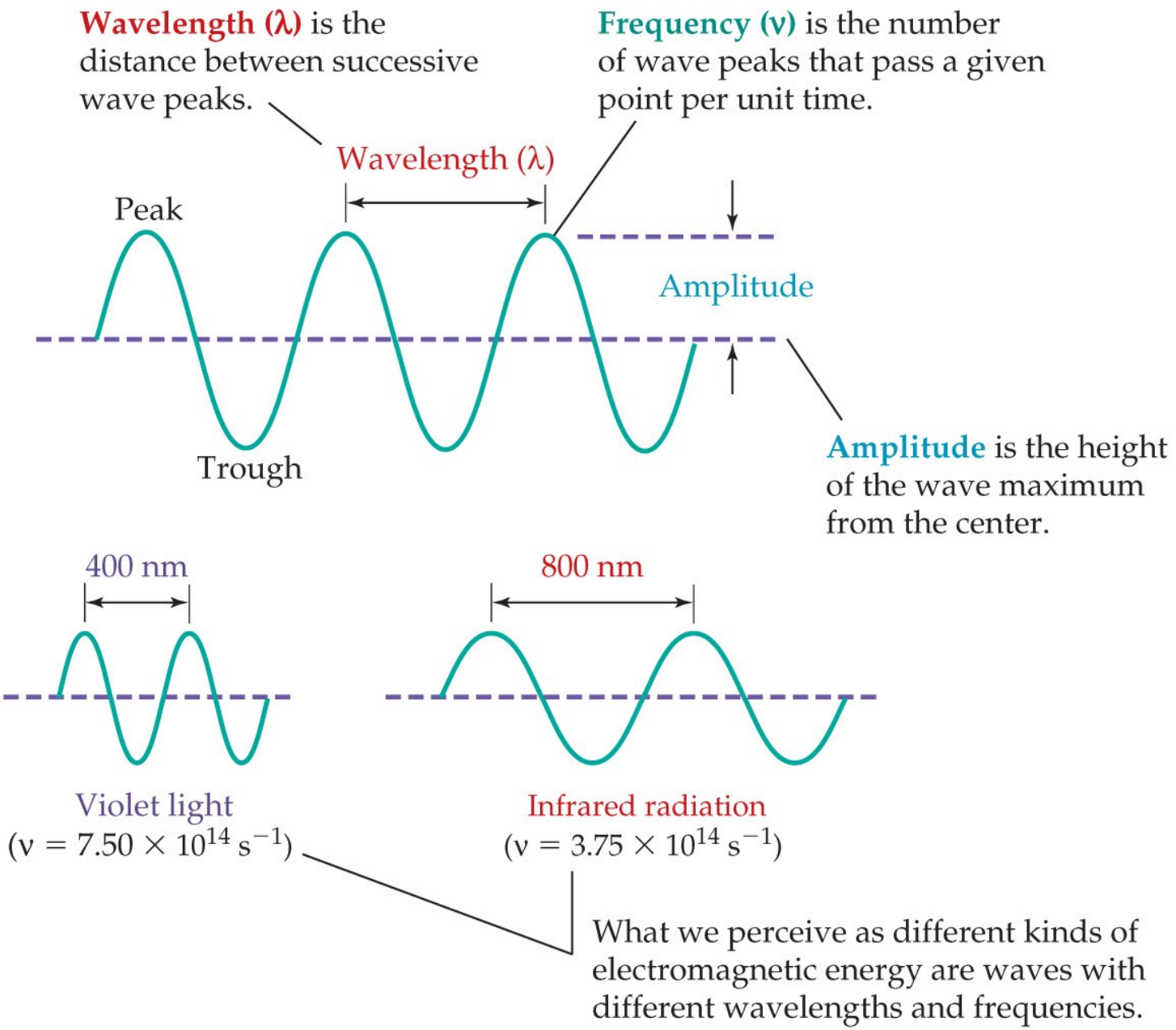
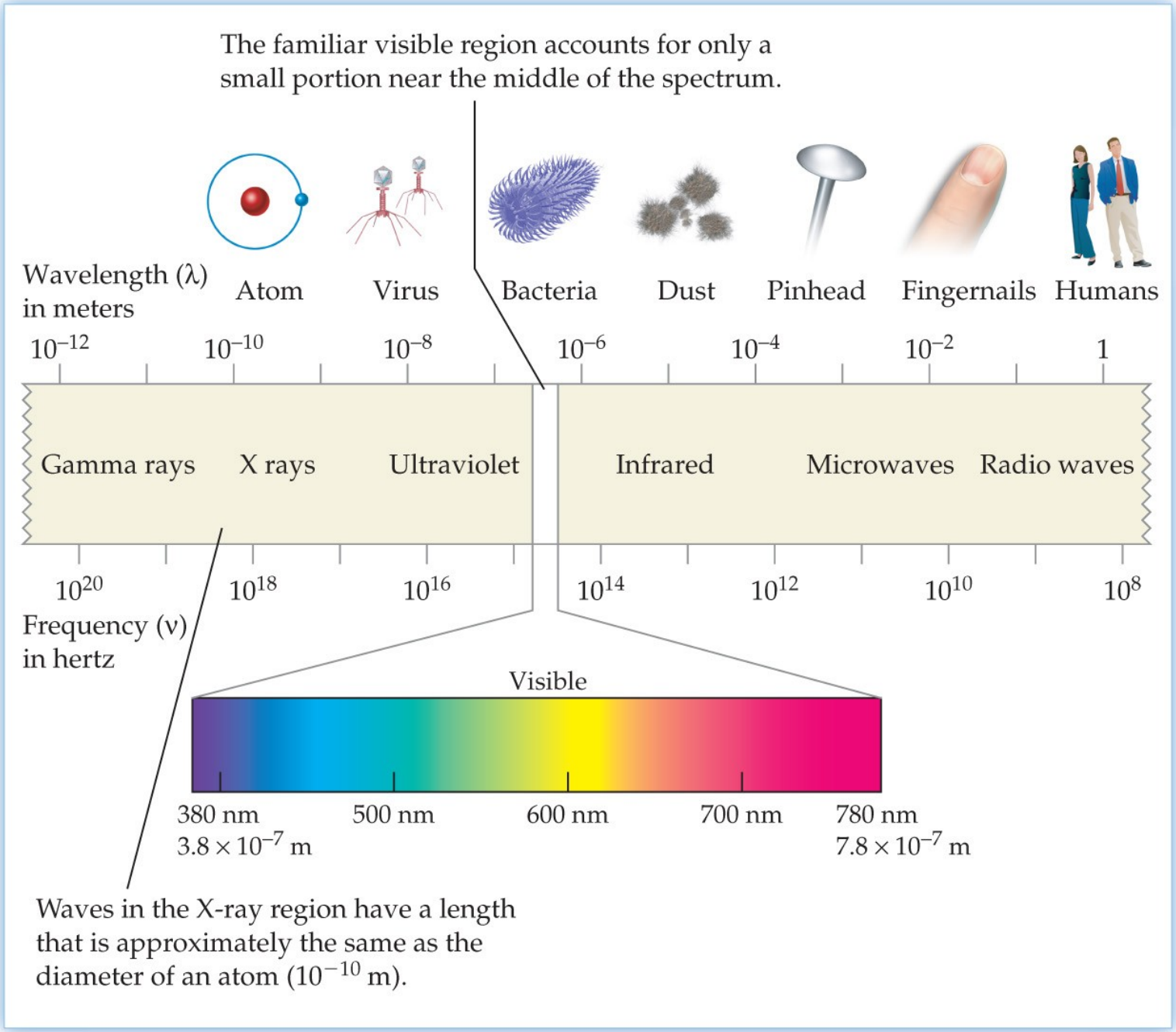
Light and the Electromagnetic Spectrum

Electromagnetic energy ("light") is characterized by

- **wavelength**
- **frequency**
- **amplitude**


Wavelength (λ) is the distance between successive wave peaks.
Frequency (ν) is the number of wave peaks that pass a given point per unit time.
Wavelength (λ)
Peak
Amplitude
Trough
Amplitude is the height of the wave maximum from the center.
400 nm
800 nm
Violet light
(ν = 7.50 × 10^14 s^−1)
Infrared radiation
(ν = 3.75 × 10^14 s^−1)
What we perceive as different kinds of electromagnetic energy are waves with different wavelengths and frequencies.


The familiar visible region accounts for only a small portion near the middle of the spectrum.
Wavelength (λ) in meters
Atom
Virus
Bacteria
Dust
Pinhead
Fingernails
Humans
10^{-12}
10^{-10}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
1
Gamma rays
X rays
Ultraviolet
Infrared
Microwaves
Radio waves
10^{20}
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^{8}
Frequency (ν) in hertz
Visible
380 nm
3.8×10^{-7} m
500 nm
600 nm
700 nm
780 nm
7.8×10^{-7} m
Waves in the X-ray region have a length that is approximately the same as the diameter of an atom (10^{-10} m).

Light and the Electromagnetic Spectrum

Wavelength x Frequency = Speed

$$\lambda \times \upsilon = c$$

$$\text{m} \qquad \frac{1}{\text{s}} \qquad \frac{\text{m}}{\text{s}}$$

c is defined to be the rate of travel of all electromagnetic energy in a vacuum and is a constant value—*speed of light*.

$$c = 3.00 \times 10^{8} \frac{\text{m}}{\text{s}}$$

Light and the Electromagnetic Spectrum

The light blue glow given off by mercury streetlamps has a wavelength of 436 nm. What is the frequency in hertz?

Wavelength (λ) x Frequency (f) = Speed of light

$$\lambda \quad x \quad \upsilon \quad = \quad c$$

$$\upsilon = \frac{c}{\lambda} = \frac{\left(3.00 \times 10^{8} \frac{\cancel{m}}{s}\right)}{\left(436 \cancel{nm}\right)\left(\frac{1 \cancel{m}}{1 \times 10^{9} \cancel{nm}}\right)}$$

$$= 6.88 \times 10^{14}\ s^{-1} = 6.88 \times 10^{14}\ Hz$$

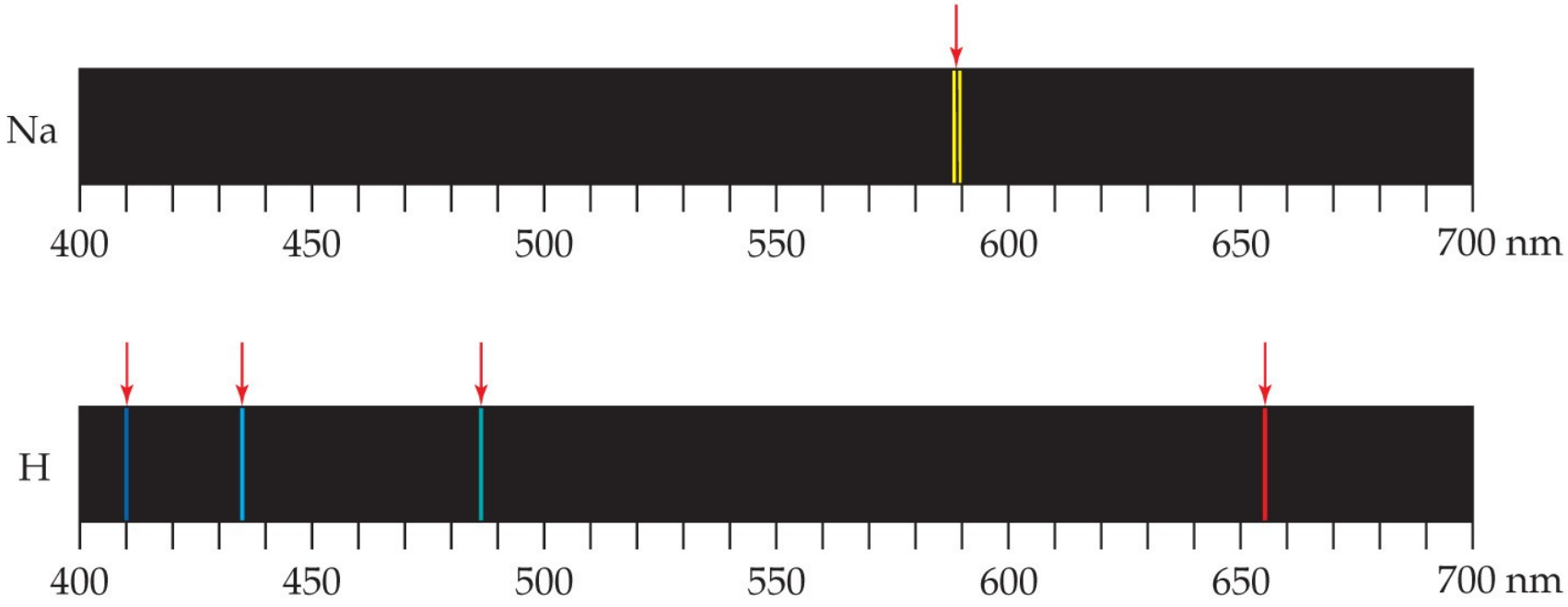
Electromagnetic Energy and Atomic Line Spectra

Excite an atom and what do you get?

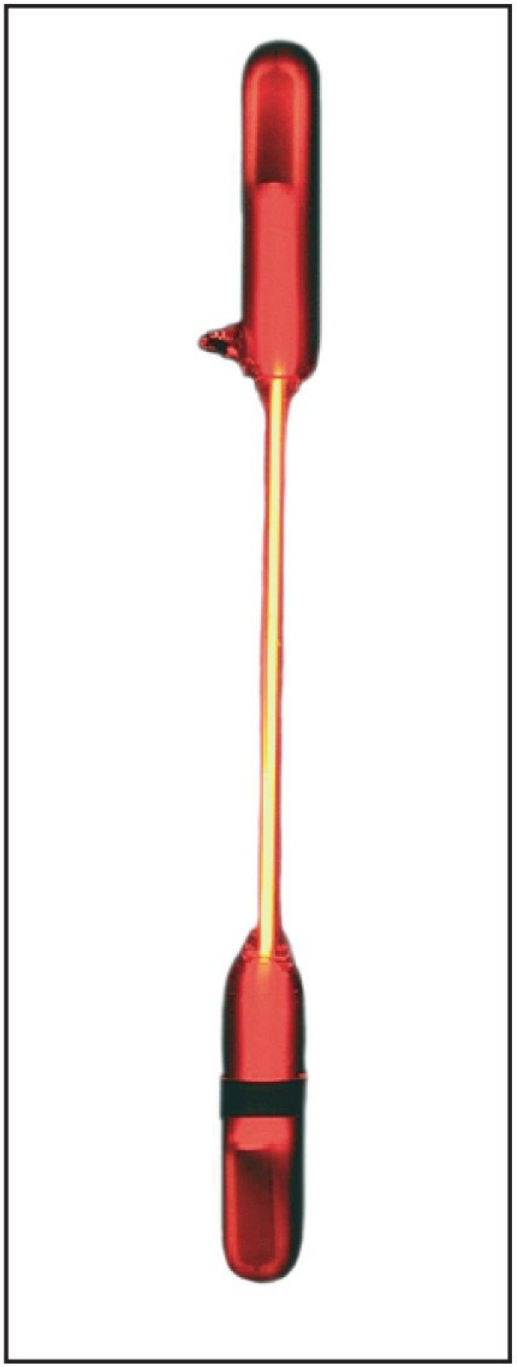
Light emission

Line Spectrum: A series of discrete lines on an otherwise dark background as a result of light emitted by an excited atom.

The visible line spectrum of energetically excited sodium atoms consists of a closely spaced pair of yellow lines.



The visible line spectrum of excited hydrogen atoms consists of four lines, from indigo at 410 nm to red at 656 nm.



Electromagnetic Energy and Atomic Line Spectra

Johann Balmer in 1885 discovered a mathematical relationship for the four visible lines in the atomic line spectra for hydrogen.

$$\frac{1}{\lambda} = R_{\infty}\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

Johannes Rydberg later modified the equation to fit every line in the entire spectrum of hydrogen. (m & n are integers where n>m)

$$\frac{1}{\lambda} = R_{\infty}\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

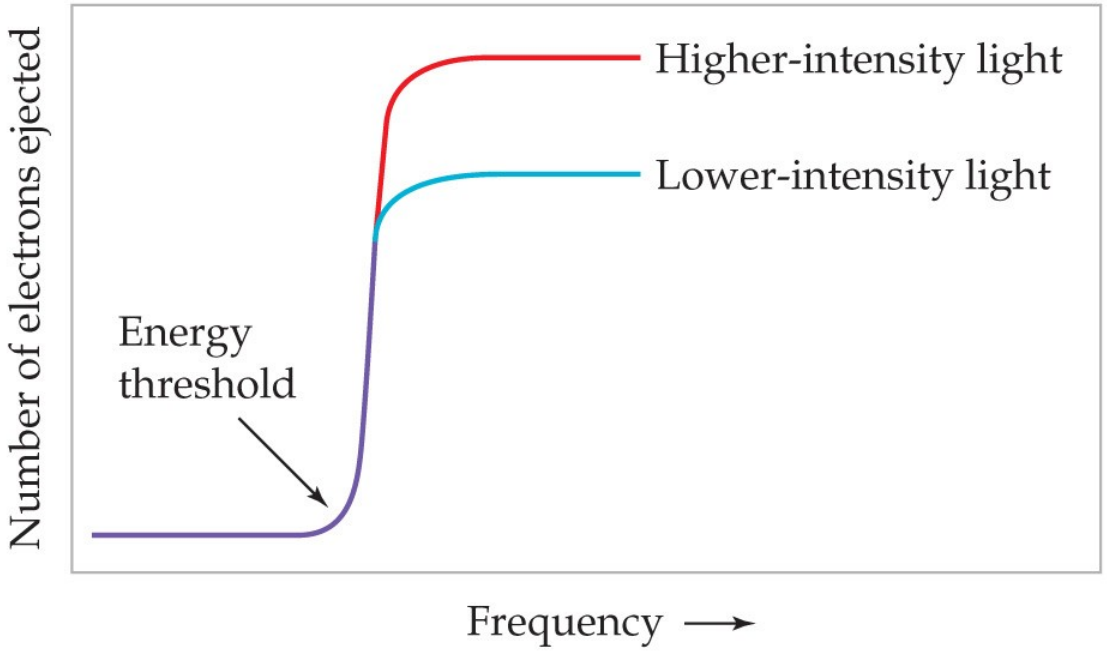
R (Rydberg Constant) = 1.097×10^{-2} nm^{-1}

Particle-like Properties of Electromagnetic Energy

Photoelectric Effect: Irradiation of clean metal surface with light causes electrons to be ejected from the metal. Furthermore, the frequency of the light used for the irradiation must be above some threshold value, which is different for every metal.

Particle-like Properties of Electromagnetic Energy

A plot of the number of electrons ejected from a metal surface versus light frequency shows a threshold value.



Increasing the intensity of the light while keeping the frequency constant increases the number of ejected electrons but does not change the threshold value.

Particle-like Properties of Electromagnetic Energy

Einstein explained the effect by assuming that a beam of light behaves as if it were a stream of particles called *photons*.

Particle-like Properties of Electromagnetic Energy

$$E = h\upsilon$$

$E \uparrow \quad \upsilon \uparrow$

h (Planck's constant) = 6.626×10^{-34} J s

Electromagnetic energy (light) is **quantized**.

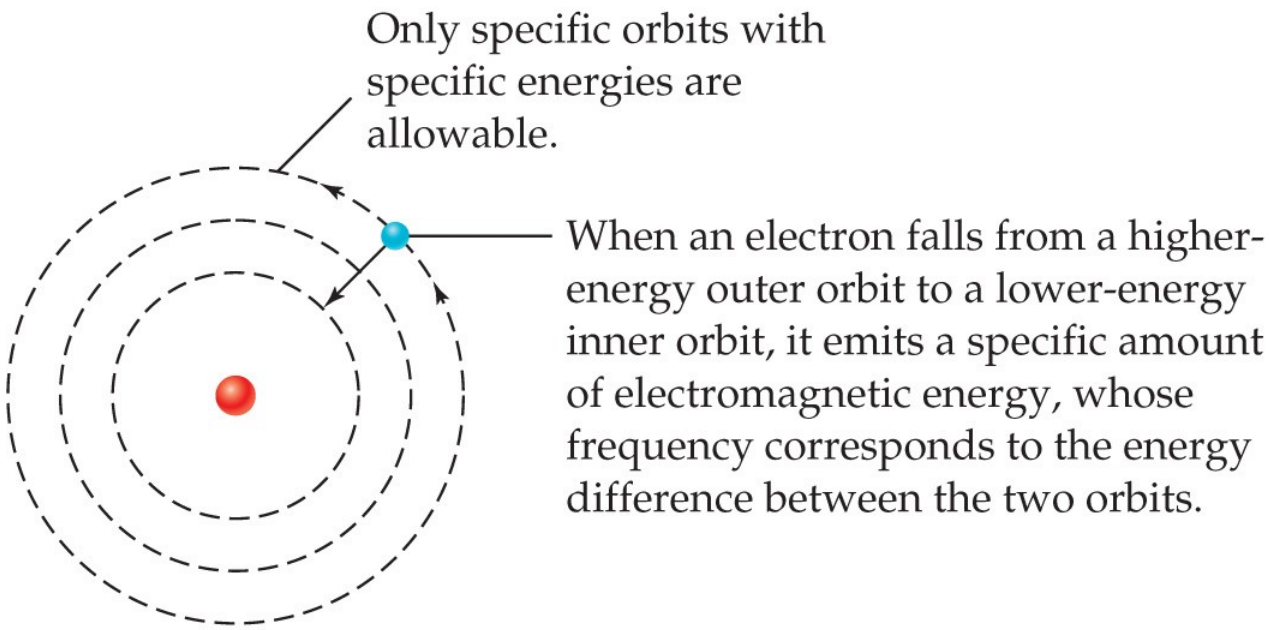
Quantum: The amount of energy corresponding to one photon of light.

Particle-like Properties of Electromagnetic Energy

Niels Bohr proposed in 1914 a model of the hydrogen atom as a nucleus with an electron circling around it.

- In this model, the energy levels of the orbits are
  "quantized"
    - that is, only certain specific orbits corresponding to certain specific energies are available for the electron.

Particle-like Properties of Electromagnetic Energy


Only specific orbits with specific energies are allowable.
When an electron falls from a higher-energy outer orbit to a lower-energy inner orbit, it emits a specific amount of electromagnetic energy, whose frequency corresponds to the energy difference between the two orbits.

Wave-like Properties of Matter

Louis de Broglie in 1924 suggested that, if *light* can behave in some respects like *matter*, then perhaps *matter* can behave in some respects like *light*.

In other words, perhaps matter is wave-like as well as particle-like.

$$\lambda = \frac{h}{mv}$$

The **de Broglie equation** allows the calculation of a "wavelength" of an electron or of any particle or object of mass m and velocity v.

Quantum Mechanics and the Heisenberg Uncertainty Principle

In 1926 Erwin Schrödinger proposed the **quantum mechanical model** of the atom which focuses on the wavelike properties of the electron.

In 1927 Werner Heisenberg stated that it is *impossible* to know precisely where an electron is and what path it follows—a statement called the **Heisenberg uncertainty principle**.

Wave Functions and Quantum Numbers

Wave equation $\xrightarrow{\text{solve}}$ Wave function or orbital (ψ) $\longrightarrow$ Probability of finding electron in a region of space (ψ^2)

A wave function is characterized by three parameters called **quantum numbers:** *n*, *l*, *m*.

Wave Functions and Quantum Numbers

Principal Quantum Number (*n*)

- Describes the size and energy level of the orbital
- Commonly called the *shell*
- Positive integer ($n = 1, 2, 3, 4, \ldots$)
- As the value of *n* increases:
  - The energy of the electron increases
  - The average distance of the electron from the nucleus increases

Wave Functions and Quantum Numbers

Angular-Momentum Quantum Number (l)

- Defines the three-dimensional shape of the orbital
- Commonly called the *sub-shell*
- There are n different shapes for orbitals
  - If $n = 1$, then $l = 0$
  - If $n = 2$, then $l = 0$ or 1
  - If $n = 3$, then $l = 0$, 1, or 2

- Commonly referred to by letter (sub-shell notation)
  - $l = 0$ *s* (sharp)
  - $l = 1$ *p* (principal)
  - $l = 2$ *d* (diffuse)
  - $l = 3$ *f* (fundamental)

Wave Functions and Quantum Numbers

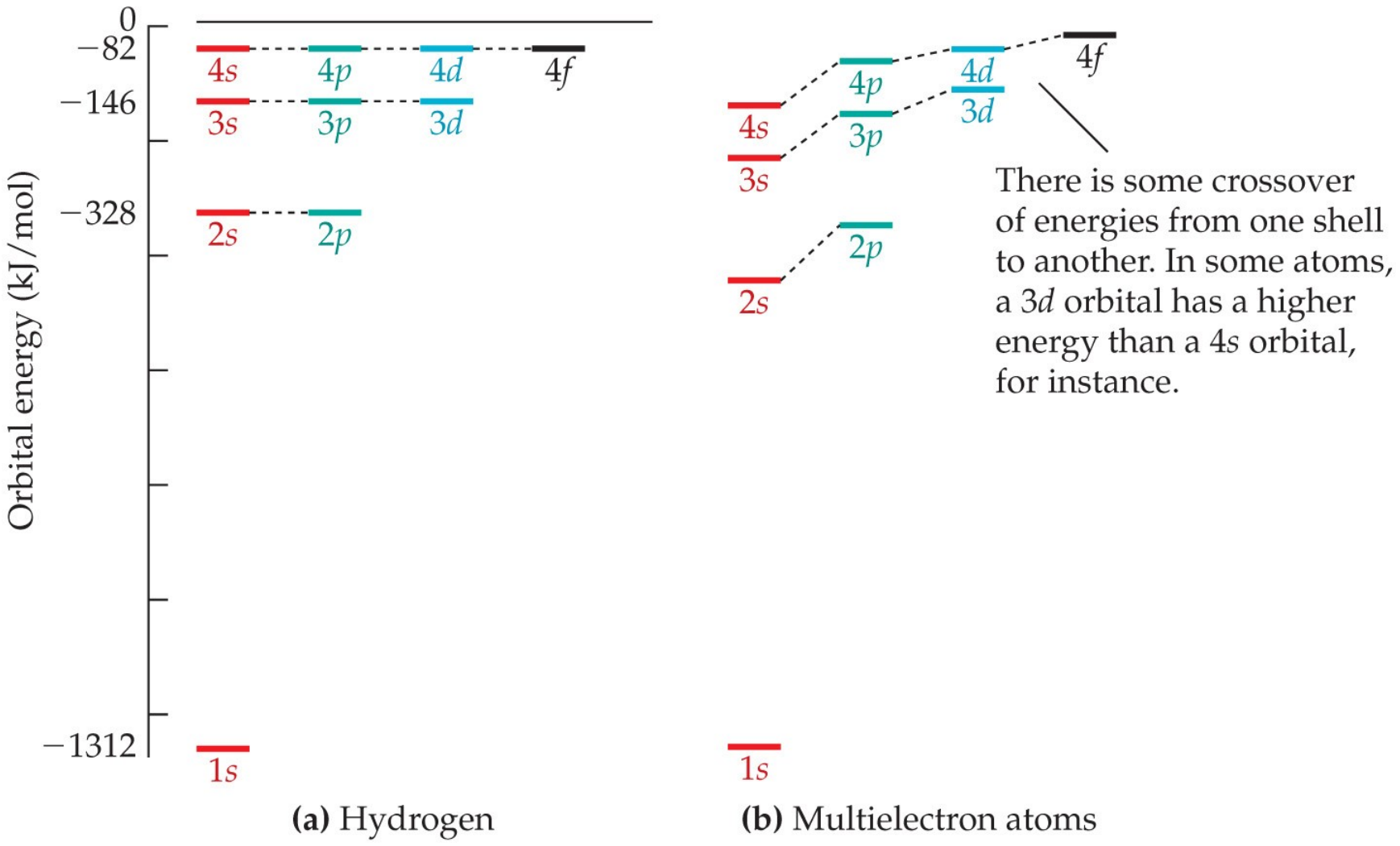
Magnetic Quantum Number (m_l)

- Defines the spatial orientation of the orbital
- There are $2l + 1$ values of m_l and they can have any integral value from $-l$ to $+l$
  - If $l = 0$ then $m_l = 0$
  - If $l = 1$ then $m_l = -1, 0,$ or 1
  - If $l = 2$ then $m_l = -2, -1, 0, 1,$ or 2
  - etc.

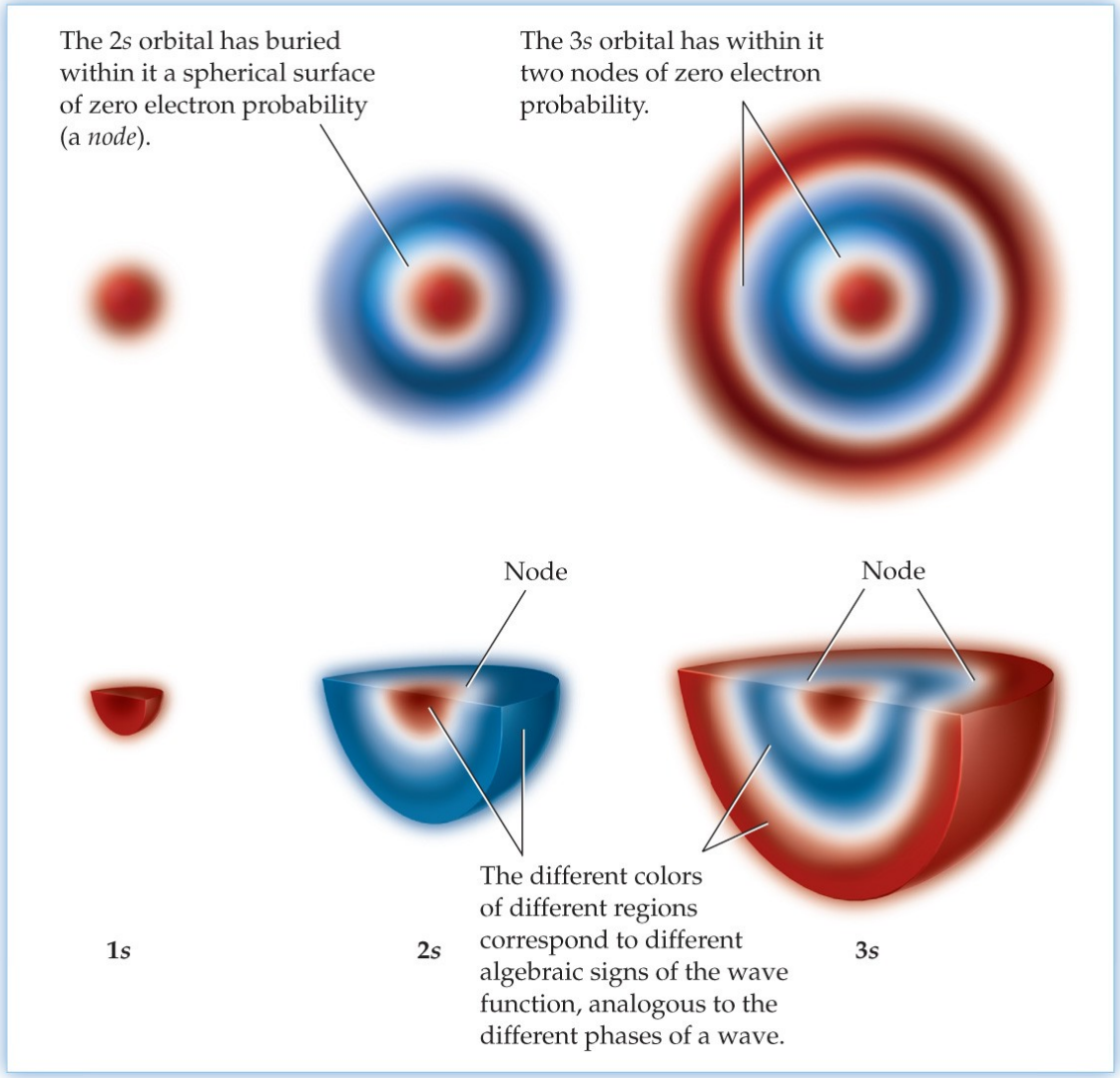
Wave Functions and Quantum Numbers

TABLE 3.1 Allowed Combinations of Quantum Numbers n, l, and m_l for the First Four Shells

n	l	m_l	Orbital Notation	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	0	1s	1	1
2	0	0	2s	1	4
	1	−1, 0, +1	2p	3	
3	0	0	3s	1	9
	1	−1, 0, +1	3p	3	
	2	−2, −1, 0, +1, +2	3d	5	
4	0	0	4s	1	16
	1	−1, 0, +1	4p	3	
	2	−2, −1, 0, +1, +2	4d	5	
	3	−3, −2, −1, 0, +1, +2, +3	4f	7	

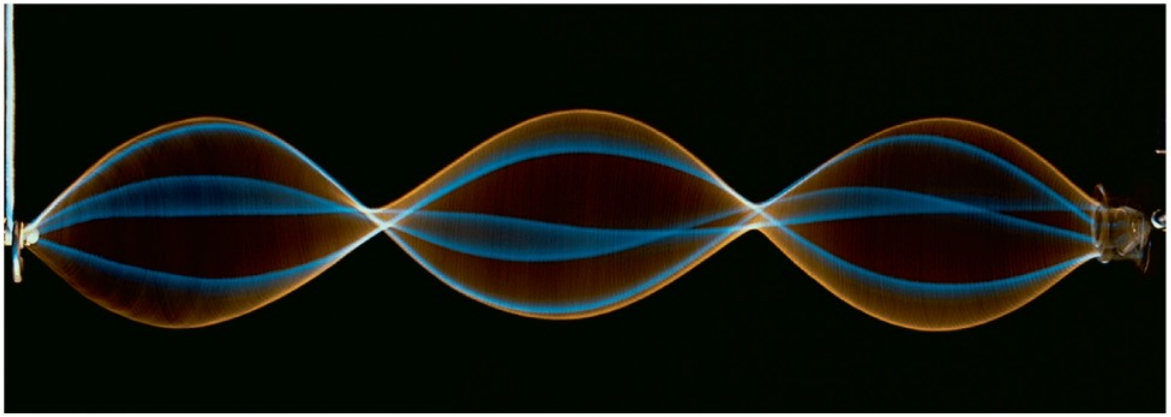

0
−82
−146
−328
−1312
Orbital energy (kJ/mol)
4s
4p
4d
4f
3s
3p
3d
2s
2p
1s
(a) Hydrogen
4s
4p
4d
4f
3s
3p
3d
2p
2s
1s
(b) Multielectron atoms
There is some crossover of energies from one shell to another. In some atoms, a 3d orbital has a higher energy than a 4s orbital, for instance.

The Shapes of Orbitals

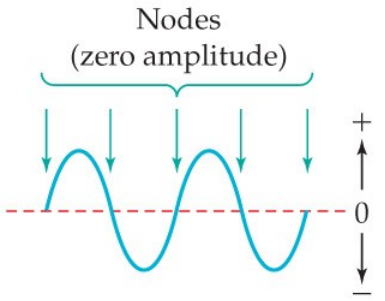

The 2s orbital has buried within it a spherical surface of zero electron probability (a node).
The 3s orbital has within it two nodes of zero electron probability.
Node
Node
The different colors of different regions correspond to different algebraic signs of the wave function, analogous to the different phases of a wave.
1s
2s
3s

Node: A surface of zero probability for finding the electron.

The Shapes of Orbitals



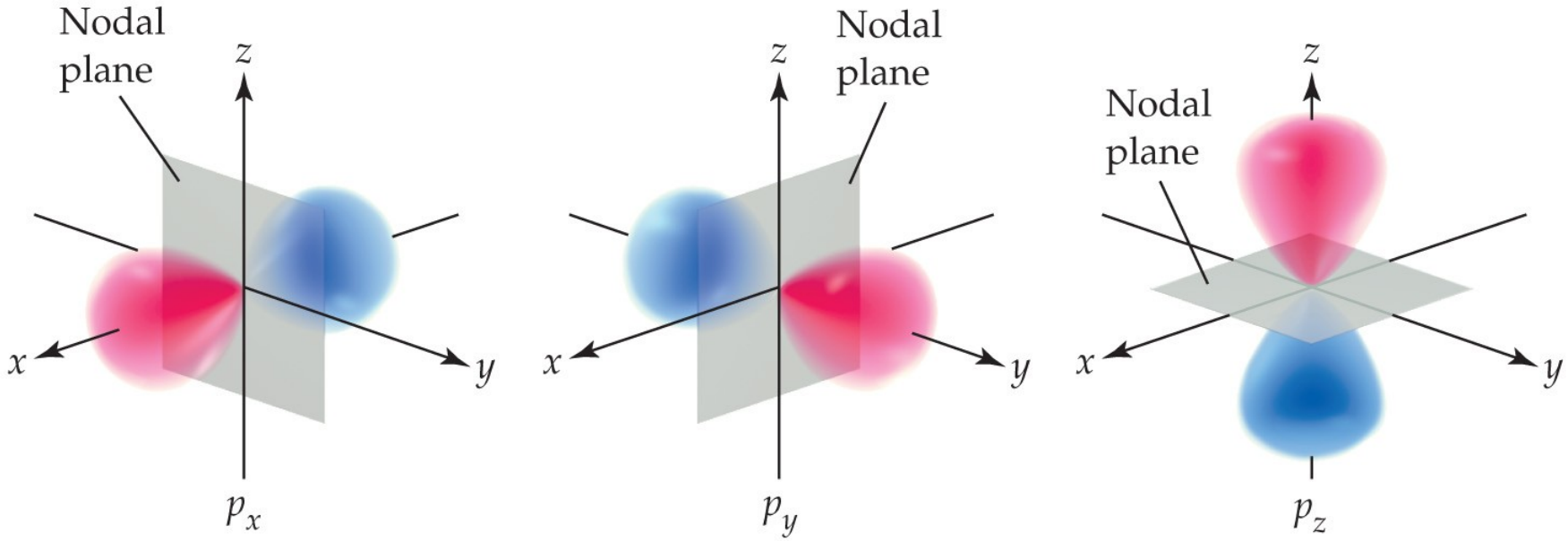
When a rope is fixed at one end and vibrated rapidly at the other, a standing wave is generated.



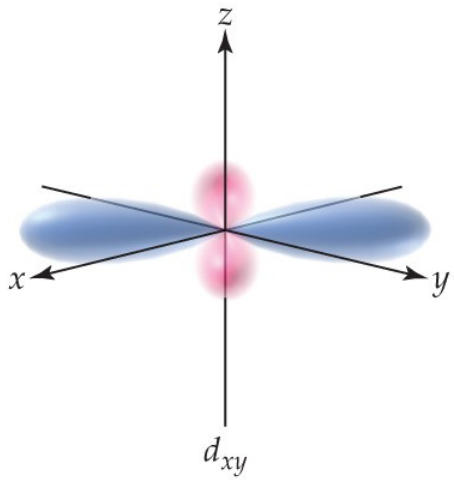
The wave has two phases with different algebraic signs, + and −, separated by zero-amplitude regions, called *nodes*.

The Shapes of Orbitals

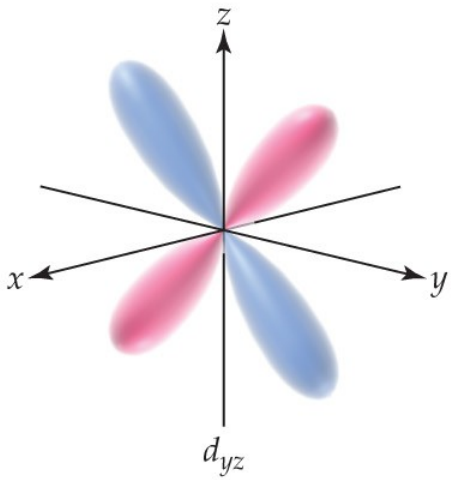
Each p orbital has two lobes of high electron probability separated by a nodal plane passing through the nucleus.



The different colors of the lobes represent different algebraic signs, analogous to the different phases of a wave.



(a)



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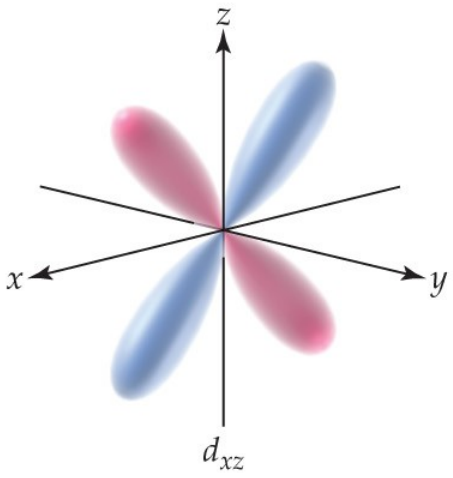
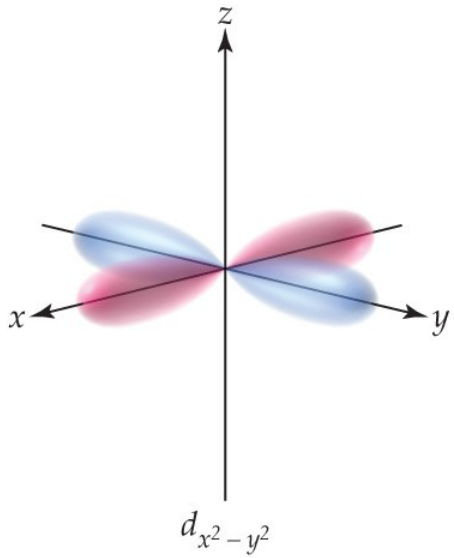
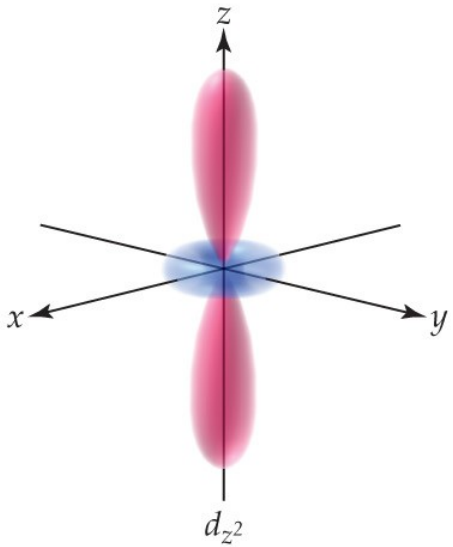


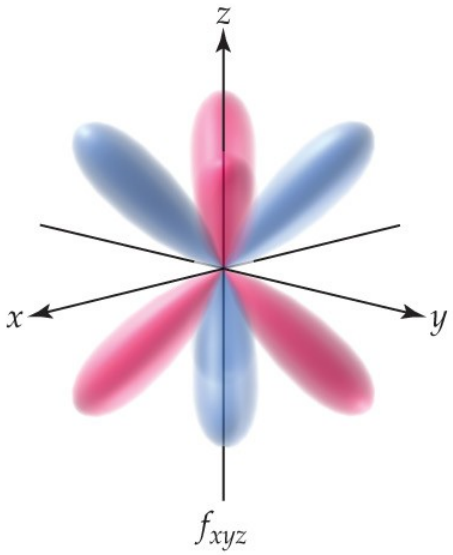
(c)



(d)

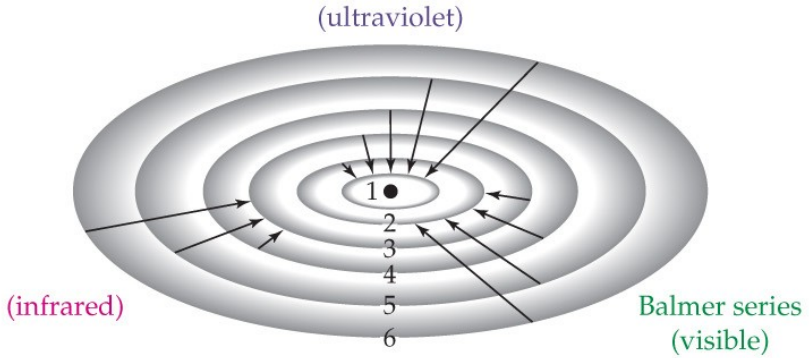


(e)

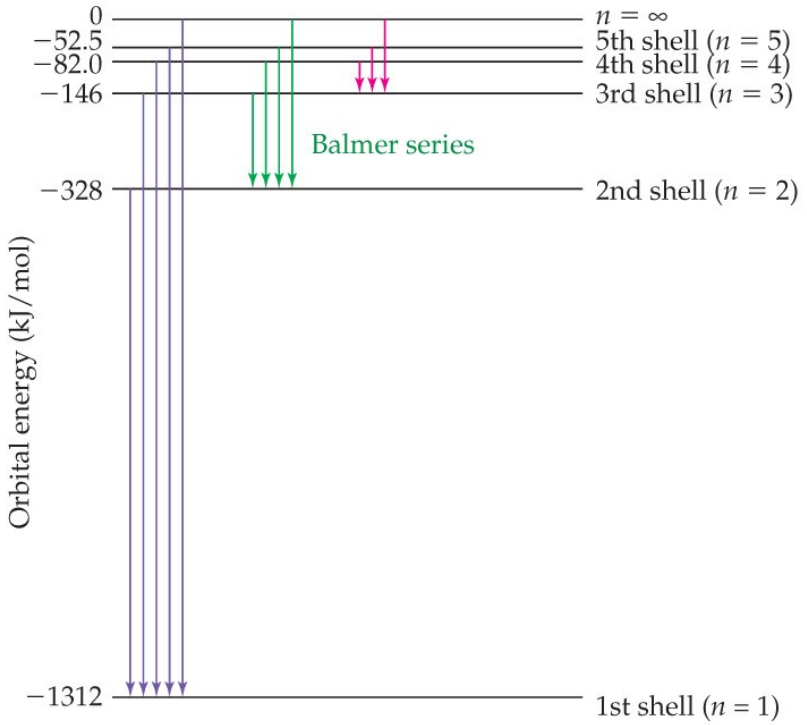


(f)

Quantum Mechanics and Atomic Line Spectra



When an electron falls from a higher-energy outer-shell orbital to a lower-energy inner-shell orbital, it emits electromagnetic energy whose frequency corresponds to the energy difference between the orbitals.



The different spectral series correspond to electronic transitions from outer-shell orbitals to different inner-shell orbitals.

Quantum Mechanics and Atomic Line Spectra

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

Shell the transition is *to* (inner-shell)

Shell the transition is *from* (outer-shell)

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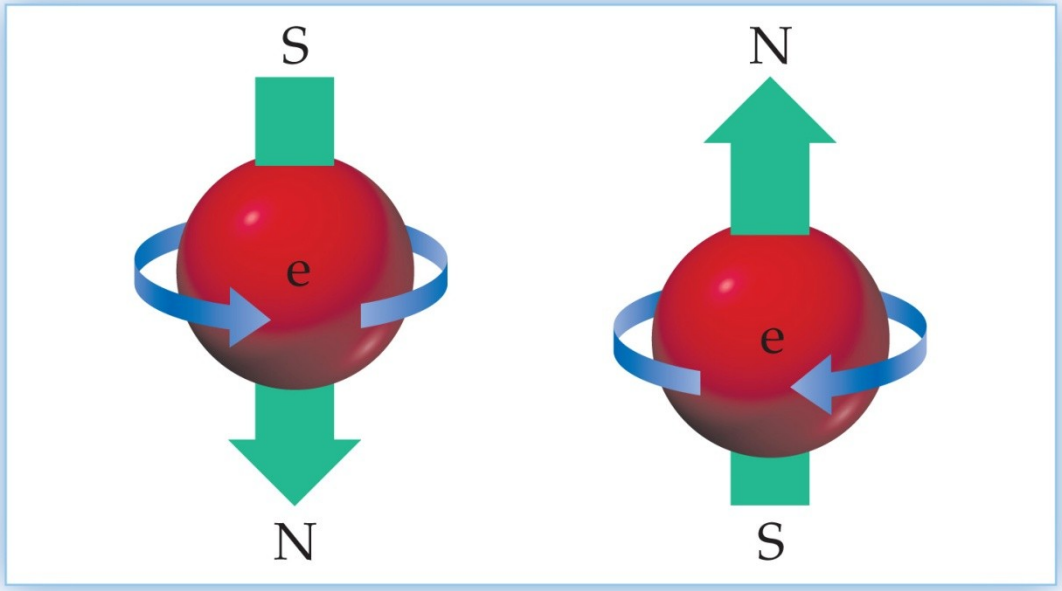
Electron Spin and the Pauli Exclusion Principle

Electrons have spin which gives rise to a tiny magnetic field and to a **spin quantum numb**



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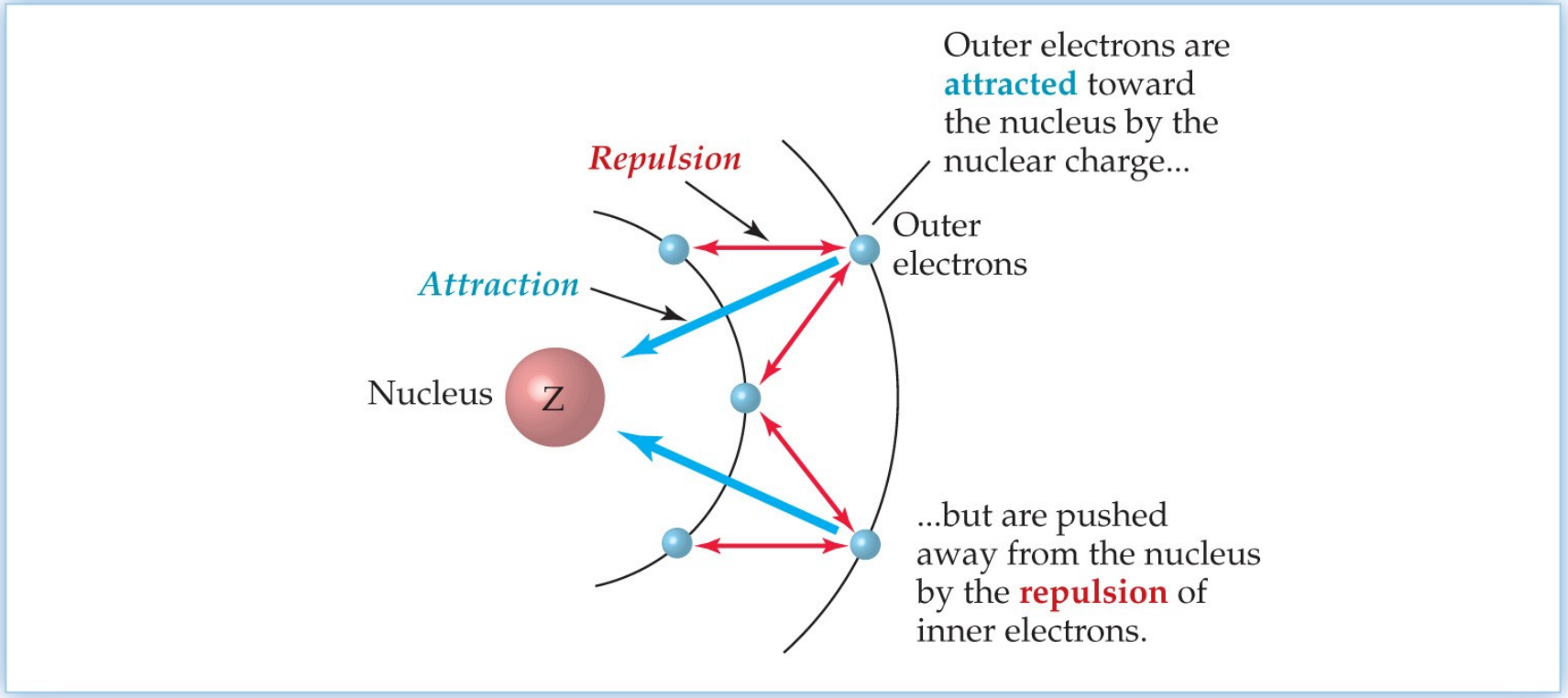
Pauli Exclusion Principle: No two electrons in an atom can have the same four quantum numbers.

Orbital Energy Levels in Multi-electron Atoms

Effective Nuclear Charge (Z_{eff}): The nuclear charge actually felt by an electron.

$$Z_{eff} = Z_{actual} \text{ - Electron shielding}$$


Outer electrons are attracted toward the nucleus by the nuclear charge...
Repulsion
Outer electrons
Attraction
Nucleus
Z
...but are pushed away from the nucleus by the repulsion of inner electrons.

Electron Configurations of Multi-electron Atoms

Electron Configuration: A description of which orbitals are occupied by electrons.

Degenerate Orbitals: Orbitals that have the same energy level. For example, the three *p* orbitals in a given subshell.

Ground-State Electron Configuration: The lowest-energy configuration.

Aufbau Principle ("building up"): A guide for determining the filling order of orbitals.

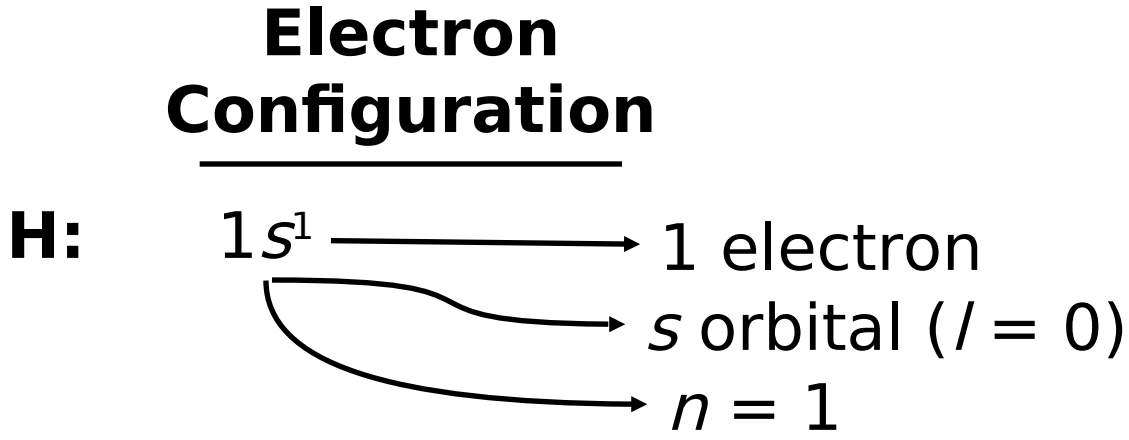
Electron Configurations of Multi-electron Atoms

Rules of the aufbau principle:

1. Lower-energy orbitals fill before higher-energy orbitals.
2. An orbital can only hold two electrons, which must have opposite spins (Pauli exclusion principle).
3. If two or more degenerate orbitals are available, follow Hund's rule.

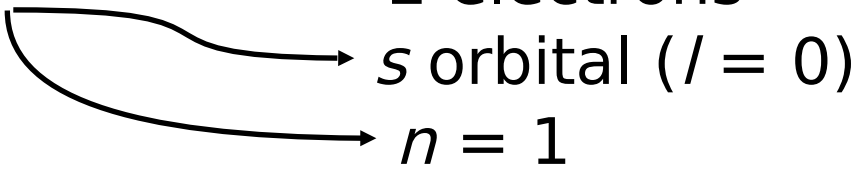
Hund's Rule: If two or more orbitals with the same energy are available, one electron goes into each until all are half-full. The electrons in the half-filled orbitals all have the same value of their spin quantum number.

Electron Configurations of Multi-electron Atoms



Electron Configurations of Multi-electron Atoms

	Electron Configuration
H:	$1s^1$
He:	$1s^2$



Electron Configurations of Multi-electron Atoms

Electron Configuration

H: $1s^1$

He: $1s^2$

Lowest energy to **highest** energy

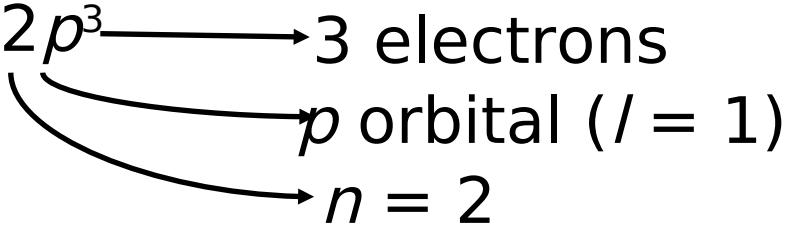
Li: $1s^2\ 2s^1$ → 1 electrons

→ s orbital ($l = 0$)

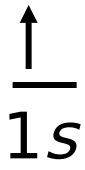
→ $n = 2$

Electron Configurations of Multi-electron Atoms

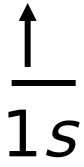
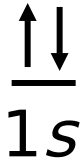
	Electron Configuration
H:	$1s^1$
He:	$1s^2$
Li:	$1s^2\ 2s^1$
N:	$1s^2\ 2s^2\ 2p^3$



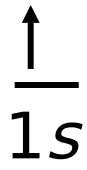
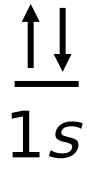
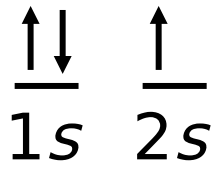
Electron Configurations of Multielectron Atoms

	Electron Configuration	Orbital-Filling Diagram
H:	$1s^1$	
He:	$1s^2$	
Li:	$1s^2\ 2s^1$	
N:	$1s^2\ 2s^2\ 2p^3$	

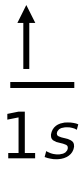
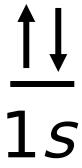
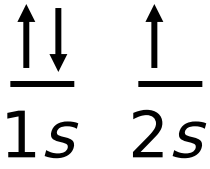
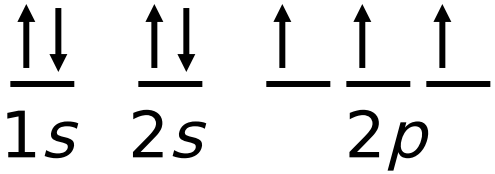
Electron Configurations of Multielectron Atoms

	Electron Configuration	Orbital-Filling Diagram
H:	$1s^1$	
He:	$1s^2$	
Li:	$1s^2\ 2s^1$	
N:	$1s^2\ 2s^2\ 2p^3$	

Electron Configurations of Multielectron Atoms

	Electron Configuration	Orbital-Filling Diagram
H:	$1s^1$	
He:	$1s^2$	
Li:	$1s^2\ 2s^1$	
N:	$1s^2\ 2s^2\ 2p^3$	

Electron Configurations of Multielectron Atoms

	Electron Configuration	Orbital-Filling Diagram
H:	$1s^1$	
He:	$1s^2$	
Li:	$1s^2\ 2s^1$	
N:	$1s^2\ 2s^2\ 2p^3$	

Electron Configurations of Multielectron Atoms

	Electron Configuration	Shorthand Configuration
Na:	$1s^2\ 2s^2\ 2p^6\ 3s^1$	[Ne] $3s^1$

Ne configuration

Electron Configurations of Multielectron Atoms

	Electron Configuration	Shorthand Configuration
Na:	$1s^2\ 2s^2\ 2p^6\ 3s^1$	[Ne] $3s^1$
P:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	[Ne] $3s^2\ 3p^3$

Electron Configurations of Multielectron Atoms

	Electron Configuration	Shorthand Configuration
Na:	$1s^2\ 2s^2\ 2p^6\ 3s^1$	[Ne] $3s^1$
P:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	[Ne] $3s^2\ 3p^3$
K:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	[Ar] $4s^1$

Ar configuration

Electron Configurations of Multielectron Atoms

	Electron Configuration	Shorthand Configuration
Na:	$1s^2\ 2s^2\ 2p^6\ 3s^1$	[Ne] $3s^1$
P:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	[Ne] $3s^2\ 3p^3$
K:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	[Ar] $4s^1$
Sc:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$	[Ar] $4s^2\ 3d^1$

Some Anomalous Electron Configurations

	Expected Configuration	Actual Configuration
Cr:	[Ar] $4s^2\ 3d^4$	[Ar] $4s^1\ 3d^5$
Cu:	[Ar] $4s^2\ 3d^9$	[Ar] $4s^1\ 3d^{10}$

Electron Configurations and the Periodic Table

Valence Shell: Outermost shell.

TABLE 3.2 Valence-Shell Electron Configurations of Main-Group Elements

Group	Valence-Shell Electron Configuration	
1A	ns^1	(1 total)
2A	ns^2	(2 total)
3A	$ns^2\ np^1$	(3 total)
4A	$ns^2\ np^2$	(4 total)
5A	$ns^2\ np^3$	(5 total)
6A	$ns^2\ np^4$	(6 total)
7A	$ns^2\ np^5$	(7 total)
8A	$ns^2\ np^6$	(8 total)

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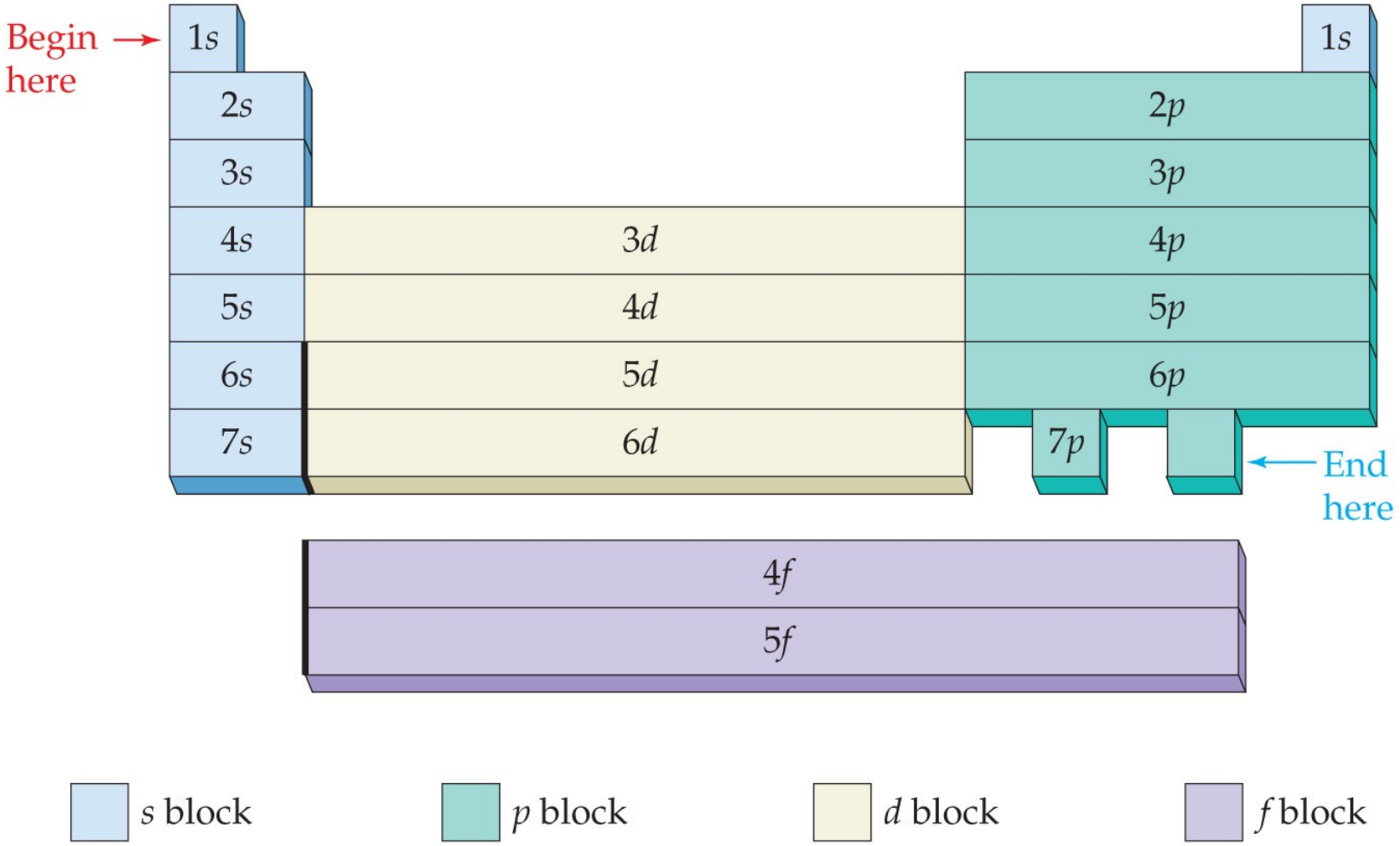
Li: $2s^1$

Na: $3s^1$

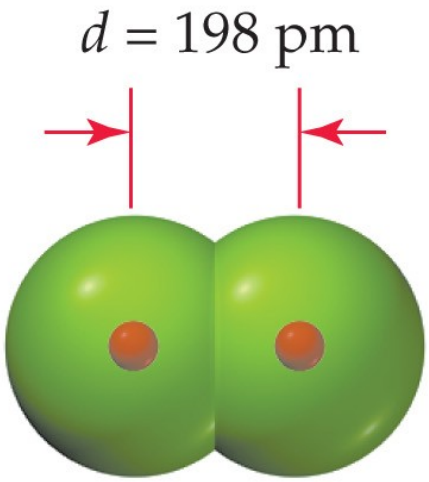
Cl: $3s^2\ 3p^5$

Br: $4s^2\ 4p^5$

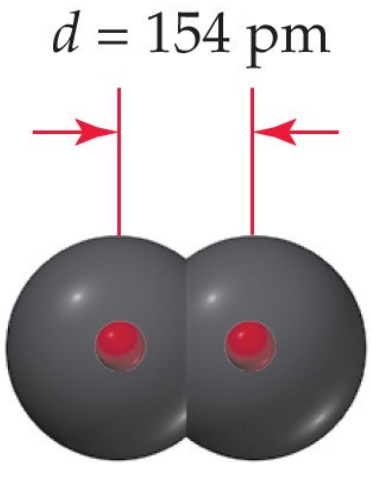
Beginning at the top left and going across successive rows of the periodic table provides a method for remembering the order of orbital filling: $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p$ and so on.



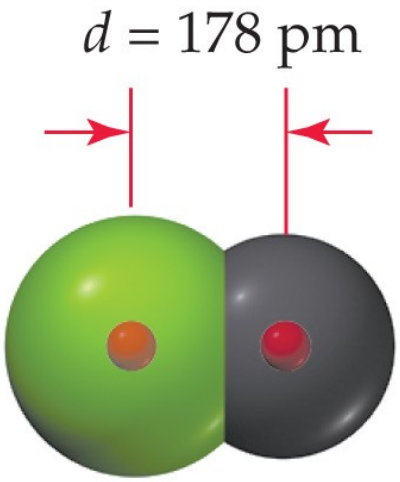
Electron Configurations and Periodic Properties: Atomic Radii



$\frac{d}{2}$ = 99 pm

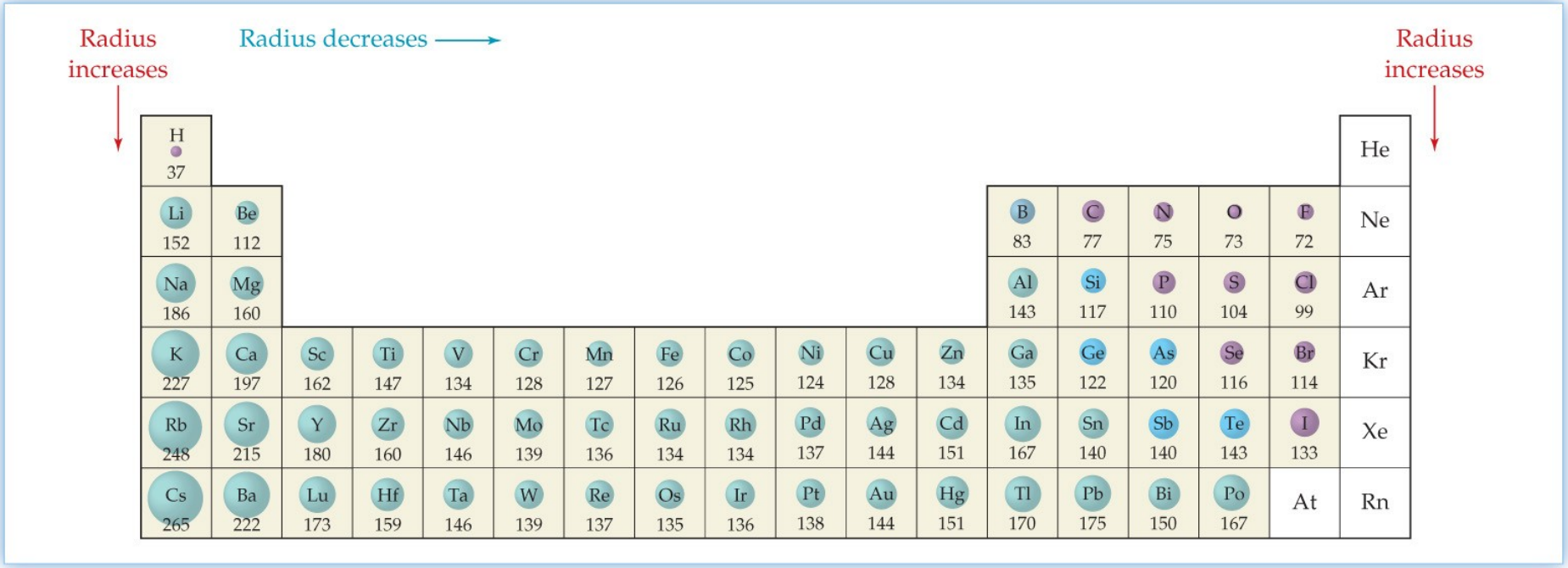


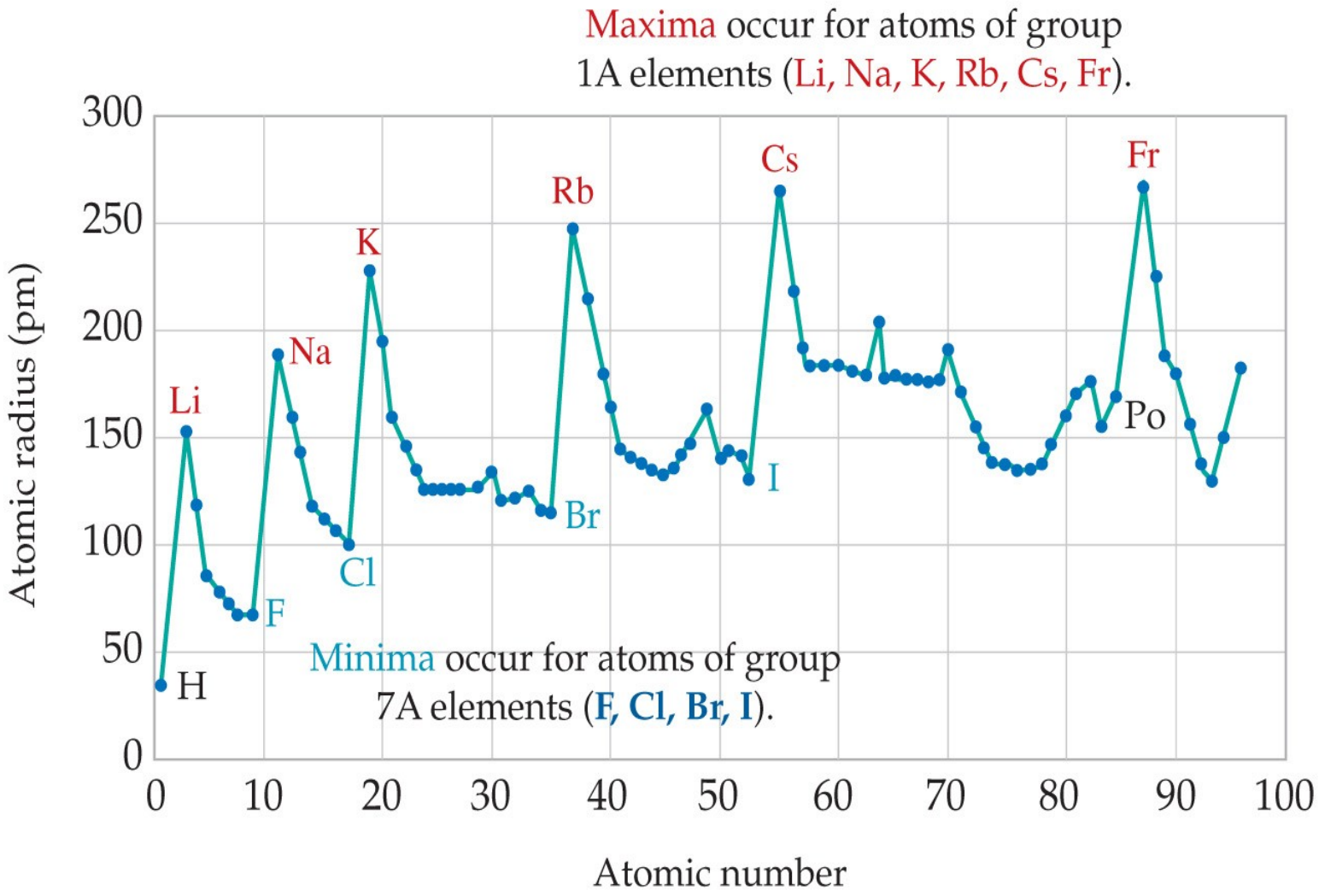
$\frac{d}{2}$ = 77 pm



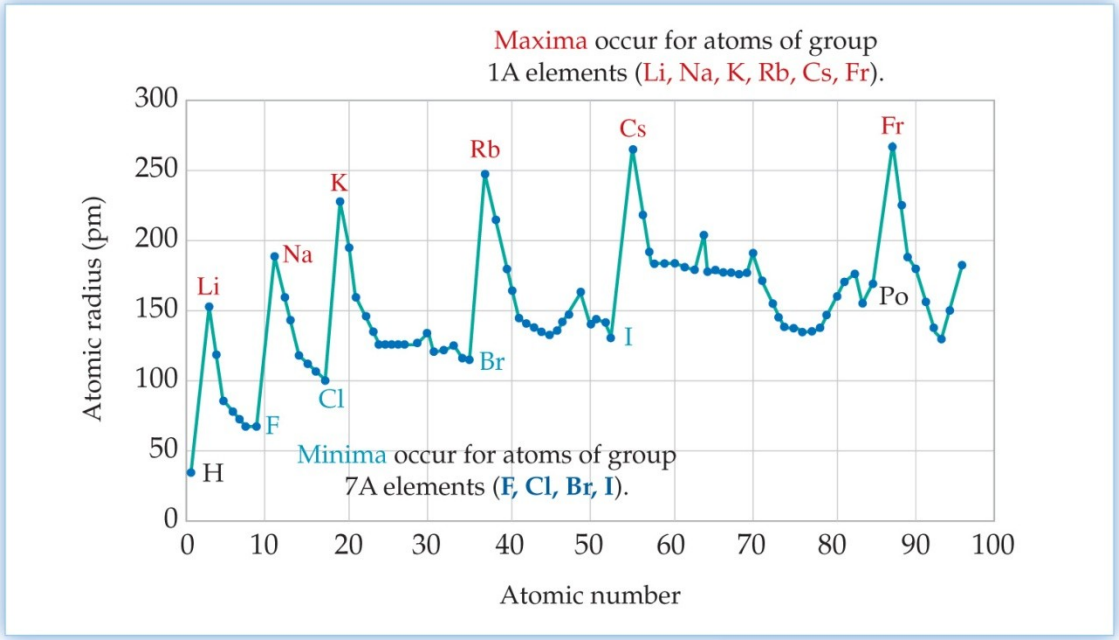
(99 pm + 77 pm = 176 pm) predicted

Electron Configurations and Periodic Properties: Atomic



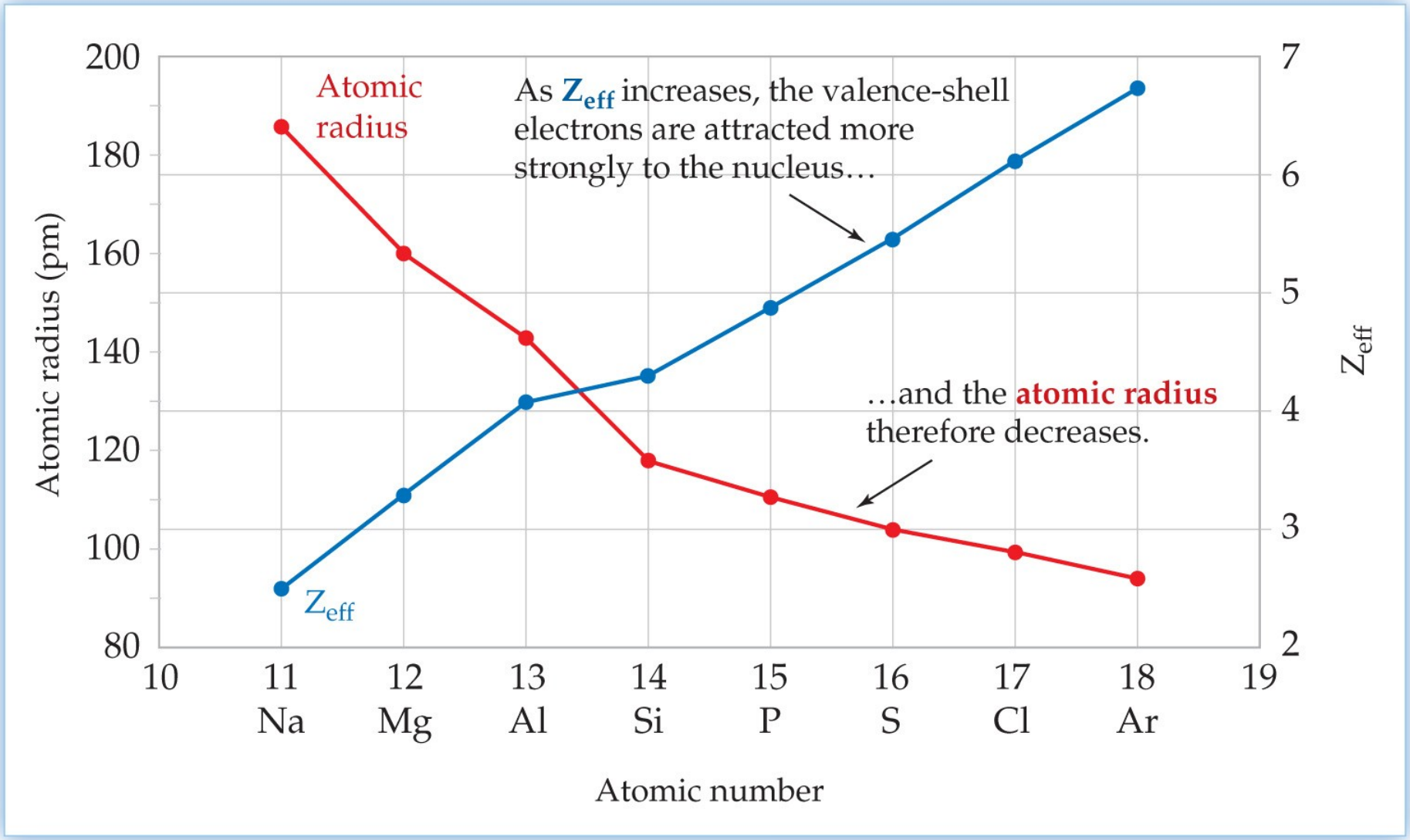

Maxima occur for atoms of group
1A elements (Li, Na, K, Rb, Cs, Fr).
Atomic radius (pm)
300
250
200
150
100
50
0
Li
Na
K
Rb
Cs
Fr
H
F
Cl
Br
I
Po
Minima occur for atoms of group
7A elements (F, Cl, Br, I).
0
10
20
30
40
50
60
70
80
90
100
Atomic number

Electron Configurations and Periodic Properties: Atomic Radii



column ↓ radius ↑

row → radius ↓


Atomic radius
As Z_{eff} increases, the valence-shell electrons are attracted more strongly to the nucleus…
…and the atomic radius therefore decreases.
Z_{eff}
Atomic radius (pm)
Z_{eff}
Atomic number
200
180
160
140
120
100
80
7
6
5
4
3
2
10
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19